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Toughening Mechanism of Liquid Crystalline Epoxy Resin with Spacers Outside the Mesogenic Group

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The toughness mechanism of the liquid crystalline epoxy resin DGE(C2-MS-C2))—which has an α-methylstilbene moiety as a mesogenic group and ethylene oxy units as spacers—cured with diaminodiphenylethane (DDEt) was investigated using time-resolved wide-angle X-ray diffraction (WAXD) measurements performed during tensile tests. The WAXD patterns of the isotropic (ISO) and LC networks of DGE(C2-MS-C2)/DDEt indicated the molecular chains in the networks were oriented along the elongation direction, with the LC network being more highly orientated than the ISO network. The dissipation energy generated during the reorientation of the network chains was proposed as the origin of the high fracture toughness of DGE(C2-MS-C2)/DDEt.

Keywords Fracture toughness; LC thermosets; liquid crystalline epoxy resin; reorientation; time-resolved WAXD; XRD

1. Introduction

It has been reported that liquid crystalline epoxy resins (LCEs) have excellent thermal and mechanical properties, such as a high glass-transition temperature (Tg), high fracture toughness, and increased bonding strength [1–8]. Their unique properties suggest that there is great potential to expand the use of epoxy resins, which are already being employed widely as encapsulants for electronics devices, as composites, and as adhesives. The origin of these unique properties of LCEs, such as their high fracture toughness, can be attributed to terms of their morphology or network structure. Ortiz et al. [2] demonstrated that a highly ordered network exhibited a higher deformation in compression tests. Lin et al. [9] researched the relationship between the curing temperature and the resulting network structure of the diglycidyl ether of 4,4′-dihydroxy-α-methylstilbene (DGEDHMS). They demonstrated that when DGEDHMS is cured at a lower temperature, a more highly layered structure is formed. These results imply that LCEs would have even more remarkably

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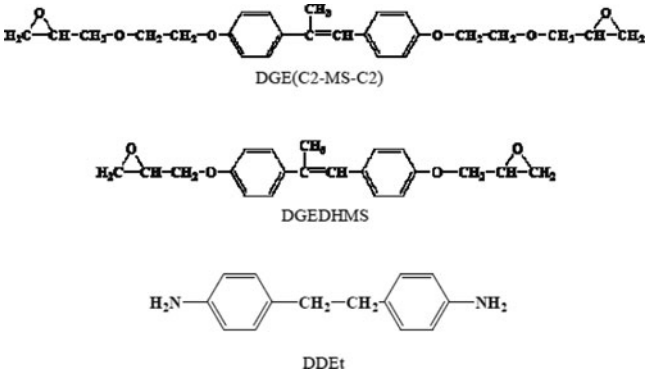


Figure 1. Chemical structures used in this study.

unique properties if they were to be cured under milder conditions, such as temperatures lower than100°C.

However, it is not easy to cure LCEs at moderately high temperature because curing at lower temperatures leads to the generation of crystalline monomers or oligomers in the system during or even before the curing reaction. A few researchers have shown that introducing spacers outside the mesogenic groups decreases the melting points of LCEs [10–15]. Broer et al. [10] and Jahromi et al. [12] synthesized LCEs with low melting points by introducing spacers outside the phenylbenzoate moiety and demonstrated that photoinitiated polymerization could occur even at low temperatures.

We had previously synthesized the LCE DGE(C2-MS-C2), whose clearing temperature is 72°C and had found that cured DGE(C2-MS-C2) exhibits a higher strain than does cured DGEDHMS, and that the LC networks of both DGE(C2-MS-C2) and DGEDHMS exhibit greater toughness than do the ISO networks of the corresponding same resin compositions [16].

In this study, we performed tensile tests using a noncontact digital video extensometer in order to evaluate the toughnesses of these networks with precision. We also performed time-resolved wide-angle X-ray diffraction (WAXD) measurements during tensile tests in order to observe the movement of the network chains. Using time-resolved X-ray diffraction analysis, Shiota et al. [17] found that the structures with a smectic-like network align in the rubbery state under static stress. However, there are few reports concerning the movement of the network chains in the glass region when an external force is applied such during a mechanical test.

In this study, the orientation behaviors of the network chains in the glass state were observed using WAXD measurements performed during tensile tests. In addition, a mechanism for the toughening exhibited by the mesogenic epoxy resin with spacers is suggested.

2. Experimental

2.1. Materials

The chemical structures of the materials used in this study are given in Fig. 1. DGE(C2-MS-C2) was synthesized as described in the literature [16]. 4,4′-Dihydroxy-α-methylstilbene (DHMS) and the diglycidyl ether of 4,4′-dihydroxy-α-methylstilbene (DGEDHMS) were

Table 1. Transition temperatures of the LCE resins

LCE resin	Heating	Cooling	
	Ti[a]	Tin[b]	Tc[c]
DGE(C2-MS-C2)	72	48	40
DGEDHMS	128	107	53

[a]Ti denotes isotropization temperature [°C].
[b]Tin denotes isotropic to nematic transition temperature [°C].
[c]Tc denotes nematic to crystal transition temperature [°C].

synthesized according to the procedures described in a patent [18]. The transition temperatures of the LC epoxy resins are listed in Table 1. Diaminodiphenylethane (DDEt) was purchased from Wako Pure Chemical Industries, Ltd. All the reagents were used without further purification.

2.2. Measurements

The Tg values were determined from the tops of the peaks of the tan δ curves obtained from dynamic mechanical analysis (DMA), which was performed using an automatic dynamic viscoelastometer (UBM DDV-25FP, A&D Company Ltd. Japan). Samples with dimensions of $30 \times 4 \times 0.4$ mm^3 were tested in the tensile mode by applying mechanical vibrations with an amplitude of 25 μm at a frequency of 10.0 Hz while raising the temperature at the rate of 2°C/min. The optical anisotropy of the cured epoxy resins was observed using an optical microscope (BH-2, Olympus Corporation, Japan) under cross-polarized light.

The tensile tests were performed as per the ISO 527–1 and 527–2 standards using a tabletop precision universal tester (Autograph AGS-J, Shimadzu, Japan) equipped with a noncontact digital video extensometer (TRViewX55S, Shimadzu, Japan); the crosshead speed was 2 mm/min. The dumbbell-shaped specimens were prepared according to type 1BB of the ISO 527–2 standard. The strain was determined as the ratio of the change in the distance between the gage marks versus the original distance. The fracture energies of the cured LCE resin systems were evaluated from the area under the stress-strain curves obtained from the tensile tests.

The time-resolved WAXD measurements made during the tensile tests were performed at the SPring 8, synchrotron radiation facility. The sample specimens were prepared according to type 1BB and then tuned to the appropriate thickness for a load cell of 5 N. The tensile tests were conducted at the crosshead speed of 6 mm/min (Fig. 2). The strain was determined by the ratio of the change in the distance between the grips that hold the test specimens versus the original distance.

The wavelength of the incident X-ray beam was 0.06 nm, and the sample-to-detector distance during the WAXD measurements was 88.5 mm. The accumulation time of each shot and the time interval between the measurements were 500 and 1350 ms, respectively. The two-dimensional (2D) WAXD patterns were detected with a flat-panel detector (C9827DK-10, Hamamatsu Photonics, Japan). The obtained WAX patterns were averaged circularly and corrected for the scattering from air and the dark current of the detector.

A dumbbell-shaped specimen was placed between the crossheads of the tensile test unit with a load cell. The tensile unit was then mounted on the synchrotron beam line.

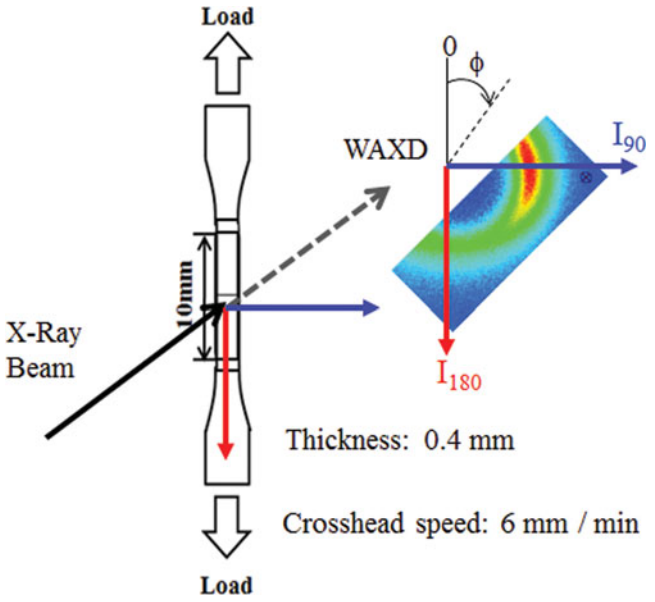


Figure 2. Scheme for experiment of time-resolved WAX measurement during the tensile test of LC epoxy resin.

The 2D data were transformed into one-dimensional (1D) analytical data by integration and averaged in a defined direction using Eq. (1).

$$I_{\phi s<\phi<\phi e}(2\theta) = \frac{1}{(\phi_e - \phi_s)} \int_{\phi s}^{\phi e} \frac{I(2\theta, \phi)}{\cos^3 2\theta} \mathrm{d}\phi \tag{1}$$

where φ is the angle clockwise from the direction of the meridian (Fig. 2) and θ denotes the Bragg angle. Further, P, which denotes the polarization factor, was assumed to be 1, and φ_s and φ_e were assumed to be $(\varphi + 5)^\circ$ and $(\varphi - 5)^\circ$, respectively.

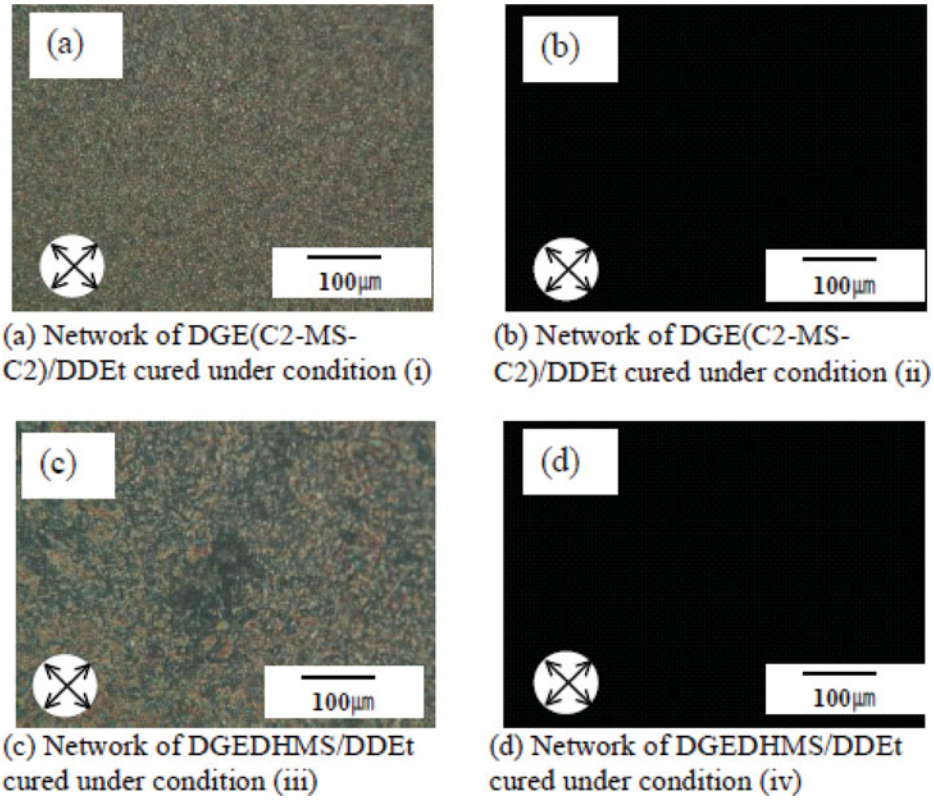
2.3. Curing of Epoxy Resins

DGE(C2-MS-C2) and DGEDHMS were cured with stoichiometric amounts of DDEt. To prepare the networks, a molten mixture of LCE and DDEt was transferred to an oven, and cured under predefined conditions. The mixture of DGE(C2-MS-C2) and DDEt was homogenized at 110°, while the mixture of DGEDHMS and DDEt was homogenized at 140°C. To prepare the LC networks, the oven temperature was kept as low as possible such that no crystals were formed in the reaction systems. The curing conditions employed, which are denoted as conditions (i) to (iv), were as follows.
DGE(C2-MS-C2)/DDEt:

(i) LC network: 90°C and 3.5 h + 170°C and 0.3 h
(ii) ISO network: 170°C and 1.5 h

DGEDHMS /DDEt:

(iii) LC network: 110°C and 2.5 h + 160°C and 0.5 h
(iv) ISO network: 160°C and 3.0 h



(a) Network of DGE(C2-MS-C2)/DDEt cured under condition (i)

(b) Network of DGE(C2-MS-C2)/DDEt cured under condition (ii)

(c) Network of DGEDHMS/DDEt cured under condition (iii)

(d) Network of DGEDHMS/DDEt cured under condition (iv)

Figure 3. POM photographs of networks of DGE(C2-MS-C2)/DDEt system and DGEDHMS/DDEt system at room temperature.

3. Results and Discussion

3.1. Network Structures Formed After Curing with DDEt

Both DGE(C2-MS-C2)/DDEt cured under condition (i) and DGEDHMS/DDEt cured under condition (iii) had an opaque appearance. Further, birefringent patterns were observed in polarized optical microscopy (POM) images of the samples (Figs. 3(a) and 3(c)). On the other hand, both resin systems when cured under conditions (ii) and (iv) had a clear appearance and did not exhibit birefringence (Figs. 3(b) and 3(d)). These results suggest that both resin composition systems produce LC networks when they are cured at lower temperatures, that is, under conditions (i) and (iii), and produce ISO networks when they are cured at higher temperatures, that is, under conditions (ii) and (iv).

The XRD patterns of the networks of DGE(C2-MS-C2)/DDEt and DGEDHMS/DDEt indicated that both the cured resins have an LC network containing a smectic-like structure, as reported in a previous paper [16]. The d-spacings calculated from the smectic peaks of DGE(C2-MS-C2)/DDEt and DGEDHMS/DDEt were 19 and 16 Å, respectively. These values were almost half the lengths of the repeating units of the resins, which include one each of the epoxy and curing agent molecules. The lengths, which were determined using Chem3D, were 37 and 32 Å, respectively. On the basis of these results, we could produce schematic illustrations of the layered structures of DGE(C2-MS-C2)/DDEt (Fig. 4) and

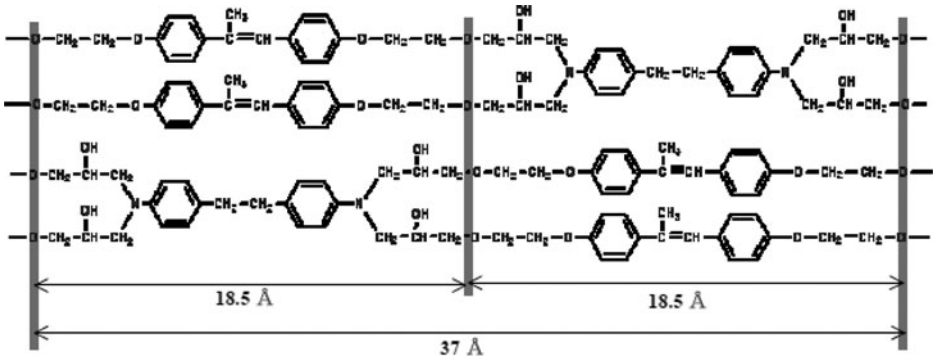


Figure 4. Proposed layered structure of DGE(C2-MS-C2) cured with DDEt in the mesophase.

DGEDHMS/DDEt (Fig. 5). We propose that a layered structure in which both methylstilbene units and diphenylethylene units exist in the same layer is formed as the lengths of the units are approximately the same. Such a layered structure is consistent with the lack of diffraction peaks corresponding to the individual units of the methylstilbene group and diphenylethylene.

Regarding the volume fraction of the layered structure, the relatively small peaks noticed in the small-angle region in the XRD patterns of DGE(C2-MS-C2)/DDEt and DGEDHMS/DDEt suggest that the volume fraction of the smectic-like phase in the network was small [16]. Therefore, we propose that these networks are composed of a major phase with a nematic-like structure and a minor phase with a smectic-like structure. Fig. 6 shows a schematic illustration of the LC network of DGE(C2-MS-C2)/DDEt. In the nematic-like structure, which forms the main phase, the mesogenic units are aligned in one direction, but are not stacked on top of each other in a single domain. On the other hand, the smectic-like structures, which form the minor phase, are dispersed in the nematic-like structure. A polydomain structure would thus be formed because none of the domains exhibits regularity in terms of the alignment direction.

3.2. Mechanical Properties

We performed the tensile tests again using a noncontact digital video extensometer in order to obtain more precise data, even though we have reported the preliminary results of the tensile tests in a previous paper [16]. The reevaluated results are shown in Fig. 7 and Table 2.

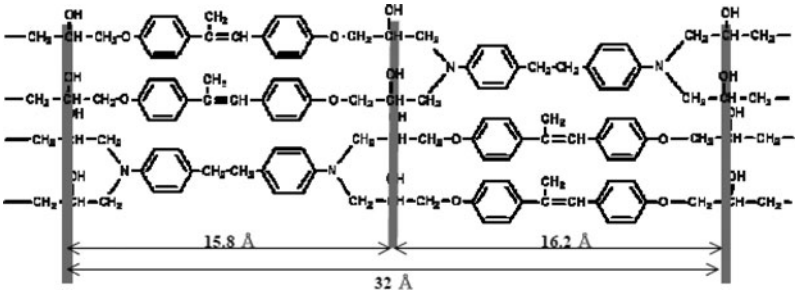


Figure 5. Proposed layered structure of DGEDHMS cured with DDEt in the mesophase.

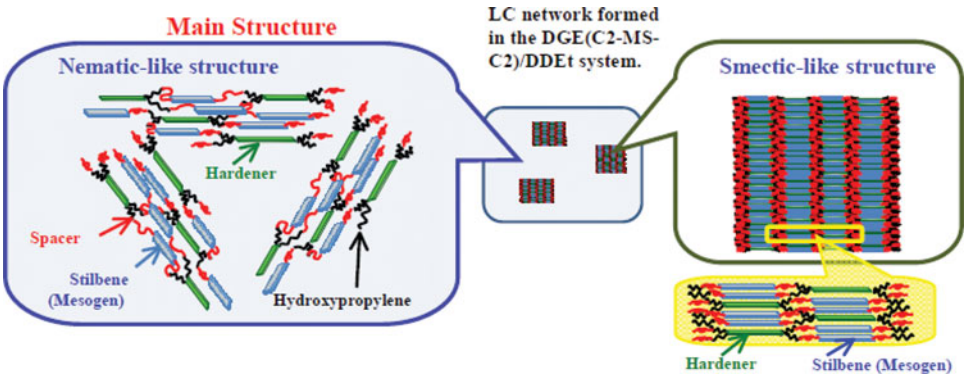


Figure 6. Schematic illustration of the LC network formed in the DGE(C2-MS-C2)/DDEt system.

The Tg values of all the examined networks were higher than 100°C (Table 2). Thus, it can be surmised that the tensile test was performed when the specimens were in their glassy state. Therefore, it is reasonable to assume that the initial moduli of all the networks are almost the same (Fig. 7). However, there are significant differences in the strains at break and fracture energies of the examined networks; the LC and ISO networks of DGE(C2-MS-C2)/DDEt have higher strains and fracture energies than those of the corresponding networks of DGEDHMS/DDEt. It would be natural to assume that these results are attributable to the flexible unit introduced in the former system. Flexible spacers would increase the mobility of the networks. Furthermore, in both the epoxy resin systems, the networks with the LC-like ordered structure exhibited higher strains and fracture energies than did the ISO networks. In the case of the DGE(C2-MS-C2)/DDEt system, the strain of the LC network is 33% and the fracture energy of the LC network is 15.8 MPa; these values are almost twice as high as those of the ISO network (16% and 7.3 MPa, respectively). The same phenomenon is also observed in the DGEDHMS/DDEt system.

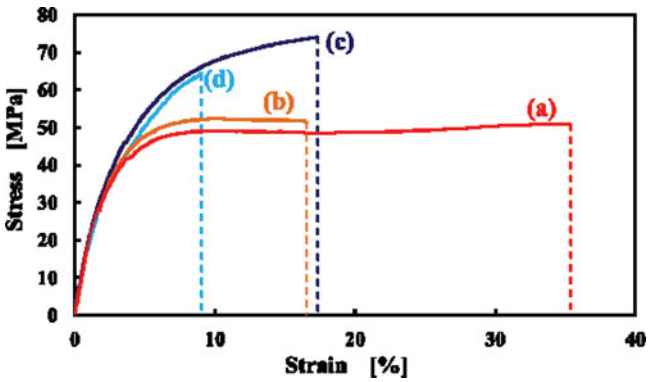


Figure 7. Stress-strain curves of the DGE(C2-MS-C2)/DDEt and DGEDHMS/DDEt systems.
(a) LC network of DGE(C2-MS-C2)/DDEt.
(b) ISO network of DGE(C2-MS-C2)/DDEt.
(c) LC network of DGEDHMS/DDEt.
(d) ISO network of DGEDHMS/DDEt.

Table 2. Tg values and tensile-test results of LCE resins cured with DDEt

Resin system	Structure	Tg	Stress at break	Strain	Fracture energy
DGE(C2-MS-C2)/DDEt	LC	100 [°C]	52 [MPa]	33 [%]	15.8 [MPa]
	ISO	106 [°C]	51 [MPa]	16 [%]	7.3 [MPa]
DGEDHMS/DDEt	LC	160 [°C]	74 [MPa]	17 [%]	9.9 [MPa]
	ISO	170 [°C]	68 [MPa]	10 [%]	4.8 [MPa]

3.3. Toughening Mechanism

Time-resolved WAXD and small-angle X-ray diffraction (SAXD) measurements were performed during the tensile tests to elucidate the toughening mechanism of the LCE resins by observing the motion of the molecular chains in the networks. Figure 8 shows the strain-stress curves obtained during the X-ray diffraction measurements. The LC network formed from in DGE(C2-MS-C2) showed exhibited greater toughness than did the LC network of DGEDHMS. The LC network of DGE(C2-MS-C2) also showed a higher strain at break and fracture energy than did the ISO network of DGE(C2-MS-C2). Although the thickness of the specimens and crosshead speed deviate from those in the ISO 527–2 standard, these results are almost consistent with the results achieved as per the standard, which are shown in Fig. 7.

The results of the time-resolved WAXD measurements are discussed because the major mechanical properties of these LC networks would be determined by the nematic-like structure. The WAXD 2D images of the LC networks of DGE(C2-MS-C2) obtained during the tensile test are shown in Figure 9. At the beginning of the tensile test, a uniform round image was observed (Fig. 9(a)), whereas, for a strain of 52%, an increase in the intensity in the direction of $\varphi = 90^\circ$ and a decrease in the intensity in the direction of $\varphi = 180^\circ$ were observed (Fig. 9(b)). The 2D WAXD data were transferred into 1D data so that they could be evaluated quantitatively; the obtained WAXD data were averaged sector wise according to the predefined direction, φ, and then corrected by transforming the thickness with the increase in the strain on the basis of the assumption that the Poisson's

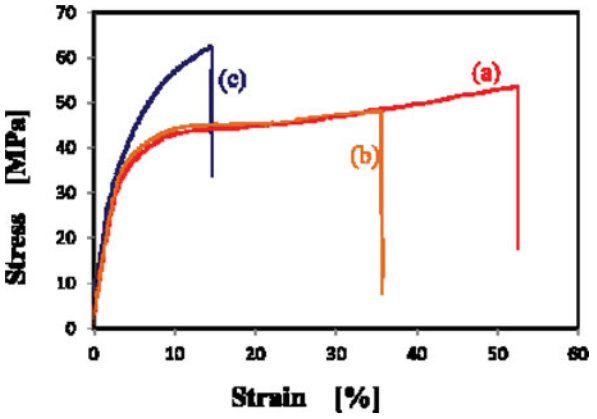


Figure 8. Stress-strain curves of (a) LC network of the DGE(C2-MS-C2)/DDEt system, (b) ISO network of the DGE(C2-MS-C2)/DDEt system, and (c) LC network of the DGEDHMS/DDEt system.

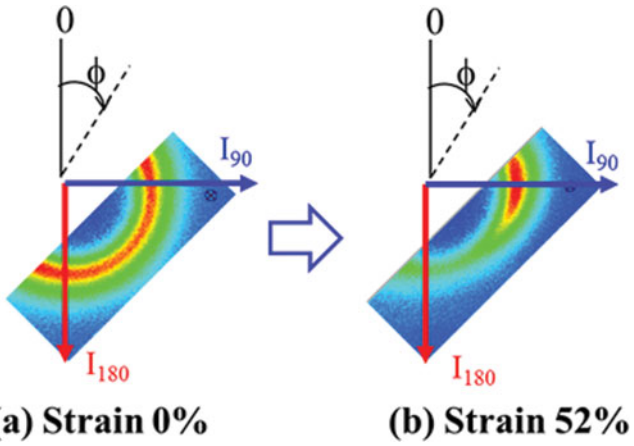


Figure 9. WAXD diffraction images corresponding to (a) 0% and (b) 52% deformation of the LC network of the DGE(C2- MS-C2)/DDEt system.

ratio is 0.33 (Fig. 10). The obtained 1D WAXD patterns are shown in Fig. 10. An increase in the intensity in the direction of $\varphi = 90^\circ$ and a decrease in the intensity in the direction of $\varphi = 180^\circ$ were observed with increasing strain. This means that the network chains were oriented along the stress direction during the tensile test.

In addition, the peak areas under each of the diffraction patterns for $\varphi = 180^\circ$ and $\varphi = 90^\circ$, which are denoted as A_{180} and A_{90}, respectively, were plotted versus the strain (Fig. 11(a)). The same analytical scheme was then applied for the ISO network of DGE(C2-MS-C2)/DDEt and the LC network of DGEDHMS/DDEt (Fig. 11(b), and Fig. 11(c), respectively). As can be seen from Fig. 11(a), the increase in A_{90} with the increase in the strain is almost equal to the decrease in A_{180} for the same process. During the initial stage of the tensile tests (Fig. 7 and Fig. 12(a)), the mesogenic groups in the DGE(C2-MS-C2)/DDEt LC network are aligned in each of the domains; however, there is no regularity between the domains. Thus, there is no macroscopic orientation. Even though

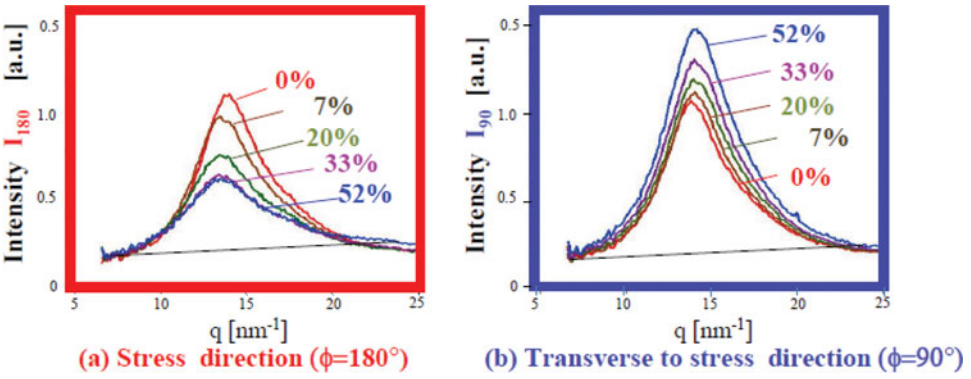


Figure 10. Transforming the WAXD pattern of the LC network of the DGE(C2-MS- C2)/DDEt as a function of the increasing strain for (a) the stress direction = 180° and (b) = 90°. The numbers in the figures denote strain values.

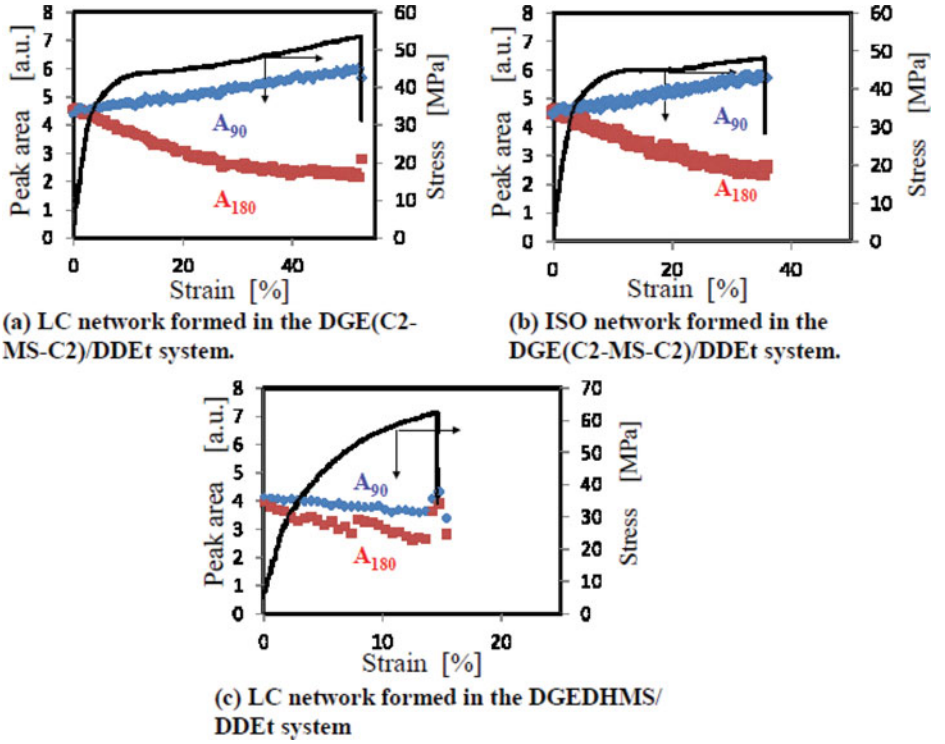


Figure 11. Change in WAX peak area versus increasing deformation.

the network is in the glass region, the mesogenic group would provide some mobility because the distance between the methylstilbene group and the crosslink point is rather large. Therefore, the methylstilbene groups in the LC network could change their directions and become oriented along the elongation direction while maintaining their alignment with the increasing strain. As a result, the network chains became macroscopically oriented

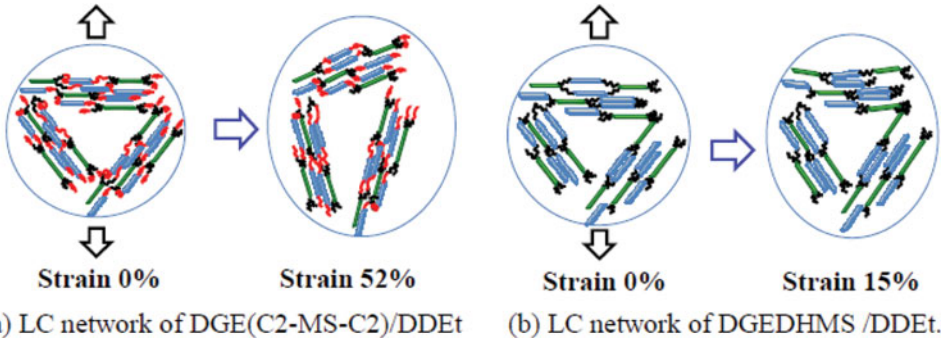


Figure 12. Schematic illustration of the change in the network structure with an increase in the strain: (a) LC network of DGE(C2-MS-C2)/DDEt and (b) LC network of DGEDHMS/DDEt.

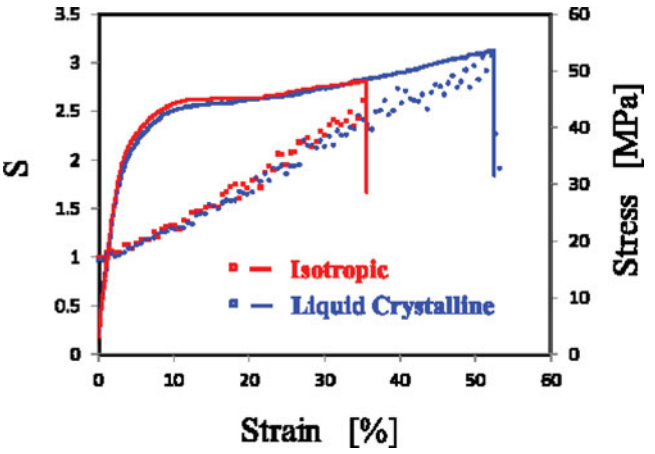


Figure 13. Orientational behavior of the LC and ISO networks of the DGE(C2-MS-C2)/DDEt system during the tensile tests.

(Fig. 12(a)). The dissipation energy, which is supposed to be generated in the above-described process, is likely responsible for the toughness for the LC network of DGE(C2-MS-C2)/DDEt.

Figure 11(b) shows that the ISO network of DGE(C2-MS-C2)/DDEt also exhibits behavior similar to that of the LC network of DGE(C2-MS-C2)/DDEt. We defined the parameter S as shown in Eq. (2) in order to be able to compare the orientation behaviors of the molecular chains in the LC and ISO networks. The dependence of S on the deformation ratio for each network is shown in Fig. 13. Figure 13 shows that, as far as the same deformation ratio is concerned, there was only a slight difference in the S values of the LC and ISO networks. It can also be seen that the LC network of DGE(C2-MS-C2)/DDEt exhibits a higher degree of orientation before the break during the tensile test.

$$S = A_{90}/A_{180} \tag{2}$$

Regarding the reasons why the LC network of DGE(C2-MS-C2)/DDEt exhibited a higher degree of orientation, we propose the following hypothesis:

(1) The LC network of DGE(C2- MS-C2)/DDEt consists of a nematic-like structure as major structure and a smectic-like structures as minor structure, as already described. It have been reported that the nematic structure is transformed into the smectic structure during the curing process; however, not the entire nematic-like structure undergoes this transform [19]. On the basis of this assumption, it is conceivable that the nematic-like structure, which includes a few smectic-like structures, might be such that the respective centers of gravity of the mesogenic groups are located close to each other. If this hypothesis is correct, the LC network DGE(C2-MS-C2)/DDEt would include a localized region that consists only of flexible molecular chains. Such a localized flexible region would exhibit remarkable deformation (Fig. 12(a)).

(2) The LC network of the DGE(C2-MS-C2)/DDEt has a nematic-like structure as well as smectic-like domains whose modules are supposed to be different. Therefore, it is likely that the applied stress disperses uniformly in the boundary regions of the domains over the entire networks. This phenomenon would prevent the generation and/or propagation

of microcracks at lower strains, which are usually initiated owing to stress concentrating at some of the structural defects. Consequently, most of the molecular chains between the cross-linking points in the LC network would undergo a higher degree of plastic deformation prior to failure. Further, they would exhibit a higher strain at break and a greater degree of orientation compared to even the ISO network formed in the same composition.

We believe that the second proposition stated above is the more probable one, because the LC networks of DGE(C2-MS-C2)/DDEt and DGEDHMS/DDEt had almost the same elastic moduli as those of the corresponding ISO network. If the mechanism described in the first proposition is dominant, it might be reasonable to expect that the elastic modulus of the LC network would be lower than that of the corresponding ISO network. However, at this stage, we do not have further data to support the second proposition.

In the case of the LC network of DGEDHMS/DDEt LC, it can be seen from Fig. 11(c) that A_{90} changes slightly compared to those for the LC and ISO networks of DGE(C2-MS-C2)/DDEt. This implies that the LC network of DGEDHMS/DDEt no longer has a sufficiently high mobility for the methylstilbene groups to change their direction towards the elongation direction; this is owing to the lack of spacers. Thus, the network would fail without exhibiting a large-scale deformation.

Conclusions

The toughening mechanism of the glass state of the LCE DGE(C2-MS-C2) cured with DDEt was studied through time-resolved WAXD measurements performed during tensile tests. The molecular chains in both the LC networks and the ISO networks of the DGE(C2-MS-C2)/DDEt system showed an orientation towards the stress direction, while the LC network of DGEDHMS/DDEt, which did not contain spacers, was only slightly oriented in this direction. A possible toughening mechanism was proposed. This mechanism assumes that the dissipation energy, which is generated during the process of molecular chain deformation during the tensile tests, is responsible for the toughness of the networks. We also proposed a layered structure, which consists of a mesogenic group and a hardener.

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The author performed the tensile tests again using a more sophisticated procedure. The obtained results are reported in this paper. The invalid formula used for calculating the strain during the tensile tests in a previous report [16] was corrected in this paper. We appreciate the advice and suggestions given during the discussions held at the 37th Annual Meeting of the Adhesion Society (2014).

The time-resolved WAXD measurements made during the tensile tests were performed at the second hutch of SPring-8 BL03XU, which has been constructed by the Advanced Soft Material Beamline Consortium (FSBL), with the proposal number 2012B7251, 2013A7201, and 2013B7251.

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